

VARIABLE TEMPERATURE EPR STUDIES OF ILLINOIS NO. 6 COAL TREATED WITH DONOR AND ACCEPTOR MOLECULES

Robert L. Thompson, Kurt S. Rothenberger, and Herbert L. Retcofsky
U. S. Department of Energy
Pittsburgh Energy Technology Center
P. O. Box 10940
Pittsburgh, PA 15236

Keywords: charge-transfer, EPR spectroscopy, coal extracts

INTRODUCTION

The structure of coal is believed to consist of extended networks of polyaromatic hydrocarbons linked by a wide variety of bonding interactions. In addition to covalent bonds, these networks contain non-covalent interactions, such as hydrogen bonding and charge-transfer interactions. Charge transfer, which can be studied by electron paramagnetic resonance (EPR) spectroscopy,¹ involves the association of electron donors and acceptors. Both donor and acceptor sites are known to exist in coal, although acceptor sites are probably far less common. Such intermolecular associations may play an important role in determining the relaxation behavior of the coal matrix in certain solvents, an important consideration in coal liquefaction.

Charge-transfer interactions between strong donors and acceptors can lead to paramagnetic products, which can be observed by EPR spectroscopy. Any unpaired electrons in the sample can interact to give coupled singlet-triplet states, or they can remain independent of each other to give doublet states. In the former case, if the triplet state lies above the singlet state, it may be too high in energy to be populated at ambient temperature; however, when the interaction lies within the appropriate range, the triplet state can become populated such that the product gives an EPR signal.¹

Most evidence to date supports the interpretation of EPR results of coal as arising from non-interacting doublet states, but some evidence in support of the existence of thermally accessible triplet states, such as temperature-dependent EPR intensities and the observation of $\Delta M_s = \pm 2$ transitions, has been reported as well.^{2,3} In this work, we have studied by variable-temperature EPR spectroscopy, Illinois No. 6 coal, its pyridine extract, and chromatographic fractions of the pyridine extract that have been treated with strong electron donors and acceptors.

The intensity of an EPR signal arising from a doublet-state spin system (I_D) is inversely proportional to temperature according to the Curie Law, whereas the intensity of an EPR signal arising from a ground-state singlet system with a thermally accessible triplet state (I_{ST}) obeys a more complex relationship. Non-Curie Law behavior is often used as a diagnostic for the latter case. We have found that a useful test for non-Curie behavior is to measure the ratio of sample intensity to that of a known doublet state sample under identical conditions. Plots of this ratio versus temperature are useful in illustrating the variable temperature EPR results, as well as accounting for changes within the spectrometer cavity and sample during the experiment.

$$\frac{I_{ST}}{I_D} = \frac{\left[\frac{C_{ST}}{T} \right] \left[\frac{4}{\exp(J/k_B T) + 3} \right]}{\left[\frac{C_D}{T} \right]} = \left[\frac{4 C'}{\exp(J/k_B T) + 3} \right] \quad (1)$$

Equation 1 shows the ideal ratio I_{ST}/I_D as a function of temperature,¹ where J is the energy gap between the singlet and triplet states and k_B is Boltzmann's constant.

EXPERIMENTAL PROCEDURES

The coal used in this work was a high-volatile bituminous coal from the Illinois No. 6 seam in Franklin County, IL (MF analyses: 72.7 %C, 4.7 %H, 1.6 %N, 1.2 %S, 8.0 %ash). The pyridine extract of this coal was obtained by Soxhlet extraction after the coal had been ground to -100 mesh. The pyridine extract was separated into functionality enriched fractions containing aromatics, bases, and acids on an activated Al_2O_3 column according to an adaptation of the procedure developed by Schiller.⁴ The yields for samples obtained from these procedures are listed in Table 1.

Samples of the coal, pyridine extract, and chromatographic fractions were treated with donors or acceptors by refluxing a mixture of coal material and reagent (in amounts ranging from 2.5:1 to 5:1) in chlorobenzene for 1 to 2 days, followed by evaporation of solvent and vacuum drying at 50°C until constant weight. Among the donors and acceptors added were tetrathiafulvalene (TTF), tetracyanoquinodimethane (TCNQ), tetracyanoethylene (TCNE), *p*-chloranil (CA), and iodine. EPR measurements were conducted as described elsewhere.⁵

RESULTS AND DISCUSSION

The treated coal and pyridine extract samples were studied by variable temperature EPR spectroscopy. Their EPR intensities were measured over a temperature range from -171°C to 23°C , then adjusted by dividing by the EPR intensities of DPPH obtained at identical temperatures.⁵ DPPH is a well-studied, stable, non-interacting doublet-state free radical that obeys the Curie Law over a wide temperature range.⁶ This method accounts for any experimental errors due to changes in sample or cavity characteristics with temperature.⁷

In every case, the EPR intensities of the coal, extract, and extract fractions increased upon treatment with the donor or acceptor, although the increase was not commensurate with a new spin for every molecule of reagent added. Neither was the magnitude of increase a function of the donor or acceptor strength of the added reagent; the acceptor with the largest electron affinity did not always give the largest intensity increase.

Only the addition of TTF, a strong donor, resulted in any discernable change in the shape of the EPR spectrum. It gave rise to a another feature at lower field to the original broad, featureless, first-derivative lineshapes of the coal and extract; all other reagents failed to alter the original lineshape. A more definitive spectrum was obtained from the CH_2Cl_2 extract taken from the TTF-pyridine extract sample. The hyperfine structure shown in Figure 1 is strikingly similar to that in the EPR spectrum of $(\text{TTF})_2(\text{BF}_4)_2$.⁸ In Figure 1, both spectra are centered at a field corresponding to $g = 2$. This spectrum is assigned to the radical cation of TTF; its detection in the extract sample implies that there are acceptor sites in the coal capable of completely removing an electron from TTF.

Variable temperature EPR studies were made of all of the treated coal samples, the results of which are shown in Figure 2. The straight, horizontal plots of $I_{\text{sample}}/I_{\text{DPPH}}$ as a function of temperature imply that all of the coal samples obey the Curie Law at least as strictly as does DPPH, establishing them as consisting predominantly of doublet-state spins. The temperature range covered was sufficiently wide to have observed any thermally accessible triplet spins, if such had existed. Because the Curie Law was so strictly observed, the newly induced spins must either be doublet state spins or have interactions so weak that they are indistinguishable from doublet state spins.

Similar EPR results were obtained for the pyridine extract samples, shown in Figure 3, and are again indicative of adherence to the Curie Law for all samples. It is significant that coal extracts have a lower spin concentration than the whole coal; thus, were a small portion of thermally accessible triplet spins present in the treated coal, but obscured by a larger portion of native doublet spins, we would expect to observe them more readily in the extract. Because we do not see any deviation from Curie Law even in the extract samples, it is clear that thermally accessible triplet spins play no important role in the EPR behavior of whole coal.

Studies supporting the deviations from Curie Law in coal samples^{2,3} have relied upon the mathematical deconvolution of EPR spectra, which is by nature artificial and rests on the questionable assumption that the lineshapes of coal signals are Lorentzian. These studies also observe forbidden $\Delta M_s = \pm 2$ transitions for certain coals. We have observed similar EPR signals in many of our samples under similar spectrometer conditions, but evidence does not support the assignment of these signals to $\Delta M_s = \pm 2$ transitions. The EPR spectra of Illinois No. 6 coal at a field corresponding to $g = 4$ are shown in Figure 4. These signals resonate at the appropriate field, but are extremely weak and their intensities do not vary with temperature. In fact, in some cases the observed signal was larger at -171°C than at 23°C , in contradiction to assignment to a thermally accessible triplet state. The location of these signals suggests that they are due to iron-bearing impurities such as kaolinite, which has been shown to possess a variety of low field signals from Fe(III) substituting in the lattice for Al(III) and Si(IV).⁹

The only non-Curie Law behavior we have observed was associated with certain minor sub-fractions from coal extract. The fractions obtained from the pyridine extract displayed weak EPR signals similar in shape to that of the coal and extract. Variable temperature EPR results for the acidic fraction revealed that it obeys the Curie Law, but the results for the aromatic and basic fractions show some slight deviation. As seen in Figure 5, their EPR intensity ratios are no longer horizontal, but slanted lines. This behavior is indicative of the presence of thermally accessible triplet spins. These fractions represent a minuscule portion of the whole coal and are likely overshadowed by the preponderance of doublet state spins.

The yields of individual fractions from the chromatographic separation were small. With this limited amount of sample, the donors and acceptors added to the fractions were limited to TTF and TCNE only. The EPR results for these treated fractions were surprising in that the aromatic sample obeyed Curie Law after treatment with TTF or TCNE, whereas the untreated aromatic fraction deviated from Curie Law. The acidic samples obeyed the Curie Law both before and after treatment with TTF or TCNE. The intensities of the treated basic samples deviated as strongly after treatment as before, particularly TTF-base, which had a curved rather than linear relationship to temperature, as shown in Figure 6.

The samples treated with TCNQ and TCNE were also studied by IR spectroscopy to monitor changes in the stretching frequency of the nitrile group, which has a frequency located in a region of the spectrum that is relatively free of absorptions for most coals. Larsen and co-workers¹⁰ have shown the location of the stretching frequency for coals treated with these two electron acceptors to be very sensitive to the amount of electron density accepted. The nitrile

stretching frequencies of these samples are summarized in Table 2, which includes TCNQ and TCNE and shows the distinct shift to lower frequencies for all of the treated coal samples.

The IR results imply that electron density is being transferred from the coal to the acceptor, but the EPR results indicate that charge-transfer complexes having thermally accessible triplet states are not being formed in any detectable quantity. Similar results have been obtained by others for coal samples treated with TCNQ.¹⁰ They have demonstrated that, although the IR frequencies of these samples were shifted, the EPR spectra did not show any evidence of formation of the TCNQ radical anion and the intensity increase was much less than would be expected if every added molecule of TCNQ resulted in an additional spin. These results were attributed to the formation of extended electronic valence bands between the coal and TCNQ.

It is possible that the frequency shifts in our samples reflect a distinct donation of electron density to TCNQ and TCNE, but the donations occur in such a way that the electrons remain paired. Alternatively, the formation of charge-transfer complexes may indeed be taking place, but with the EPR active triplet state so high in energy as to be essentially unpopulated at room temperature and below.⁵

We have found that a very small fraction of the spins present in Illinois No. 6 coal deviates from the Curie Law due to the population of thermally accessible triplet states. The vast majority of spins observable by EPR in the whole coal behaves as non-interacting doublet state spins, effectively obscuring the weak non-Curie Law behavior. We have also observed that Curie Law behavior persists even in samples treated with reagents capable of inducing charge transfer. Deviation from Curie Law finally becomes observable in the aromatic and basic fractions of the pyridine extract of the coal, as well as in some of the treated fractions. IR spectra reveal that electron density is indeed donated from the coal to the acceptors TCNQ and TCNE, and the EPR intensities are increased relative to the untreated coal samples, but treatment does not result in any noticeable deviation from Curie Law. Finally, while weak EPR signals are observed at half-field for many of the samples studied above, these signals are believed to arise from Fe(III)-containing impurities rather than from $\Delta M_s = \pm 2$ transitions.

REFERENCES

1. Bijl, D., Kainer, H., Rose-Innes, A.C. *J. Chem. Phys.* 1959, **30**, 765.
2. Duber, S., Więckowski, A.B. *Fuel* 1984, **63**, 1474.
3. Duber, S., Mikosz, J. *Fuel* 1993, **72**, 267.
4. Schiller, J.E., Mathiason, D.R. *Anal. Chem.* 1977, **49**, 1225.
5. Rothenberger, K.S., Sprecher, R.F., Castellano, S.M., Retcofsky, H.L. in 'Magnetic Resonance of Carbonaceous Solids' (Eds. R. Botto, Y. Sanada), ACS Adv. Chem. Ser. 229, Washington, DC, 1992, 581.
6. Singer, L.S., Spencer, E.G. *J. Chem. Phys.* 1953, **21**, 939.
7. Castellano, S., Chisolm, W., Sprecher, R.F., Retcofsky, H.L. *Anal. Chem.* 1987, **59**, 1726.
8. Wudl, F., Kaplan, M.L. *Inorg. Synth.* 1979, **19**, 27.
9. Angel, B.R., Hall, P.L. *Proc. Int. Clay Conf., Madrid* 1973, 47.
10. Flowers, R.A., Gebhard, L.A., Larsen, J.W., Sanada, Y., Sasaki, M., Silbernagel, B. *Energy Fuels* 1994, **8**, 1524.

Table 1. Extraction and Chromatographic Yields
(each value an average of 3 runs)

pyridine extraction yield	16.8	
chromatographic yields:	based on extract	based on coal
aromatics	4.2	0.7
bases	7.4	1.2
acids	17.3	2.9

Table 2. Infrared Frequency Changes for Samples Treated with TCNQ and TCNE

sample	$\nu(\text{CN})$	$\Delta\nu(\text{CN})$	sample	$\nu(\text{CN})$	$\Delta\nu(\text{CN})$
TCNQ	2227	----	TCNE	2236	----
coal-TCNQ	2179	-48	coal-TCNE	2200	-36
extract-TCNQ	2182	-45	extract-TCNE	2201	-35
			aromatics-TCNE	2206	-30
			bases-TCNE	2206	-30
			acids-TCNE	2213	-23

Figure 1. EPR Spectra of (a) CH_2Cl_2 Soluble Portion of Pyridine Extract + TTF and (b) $(\text{TTF})_3(\text{BF}_4)_2$.

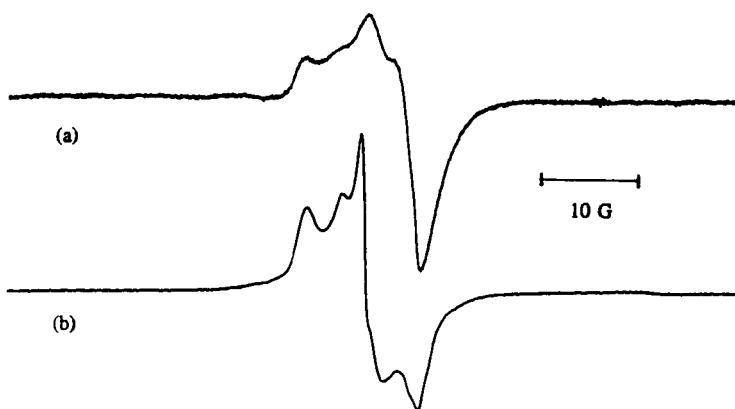


Figure 2. VT-EPR Results for Treated Illinois No. 6 Coal Samples.

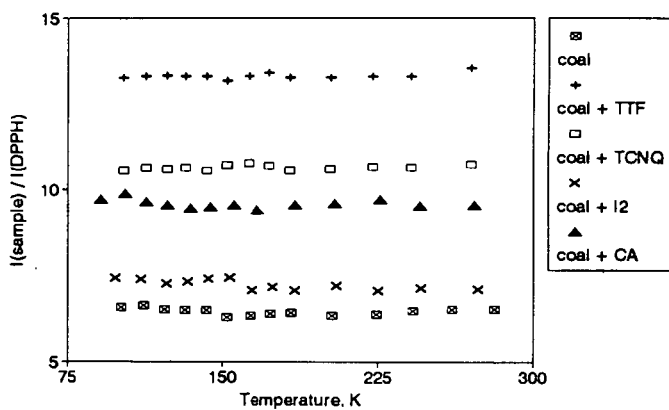


Figure 3. VT-EPR Results for Treated Pyridine Extract Samples.

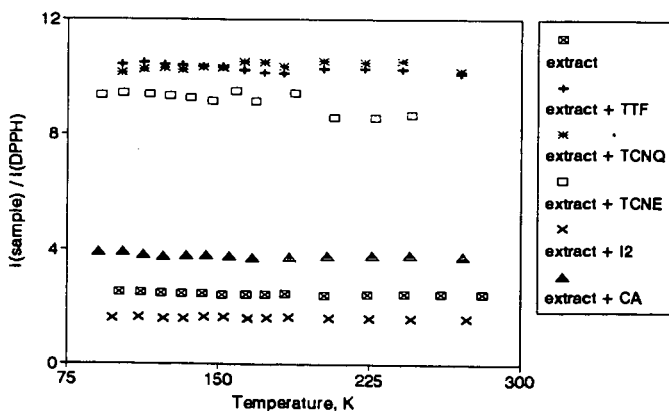


Figure 4. Half Field EPR Spectra of Illinois No. 6 Coal.

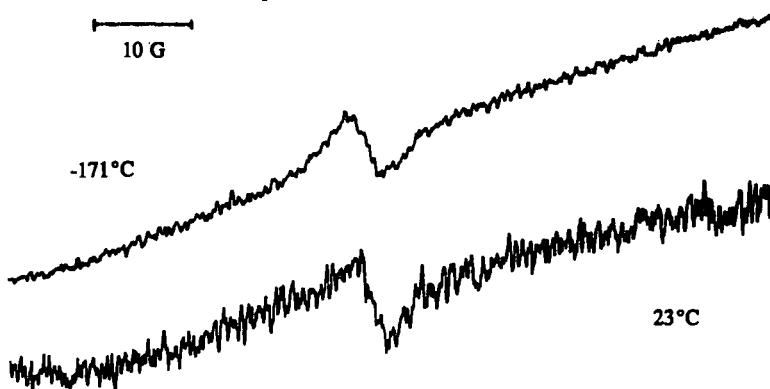


Figure 5. VT-EPR Results for Pyridine Extract Fractions..

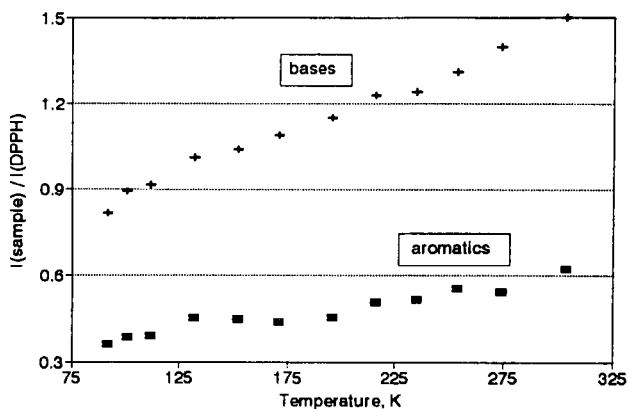


Figure 6. VT-EPR Results for Treated Base Fraction Samples.

